Synthesis and Characterization of Manganese Carboxylates

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Abstract: The explorations of prodegradant additives for plastics from trans-metals organic salts have been being conducted. This paper reports a method of synthesis of manganese carboxylates and their characterization. The new method involves reaction between molten carboxylic acid with sodium hydroxide in alcoholic solution to produce sodium carboxylate, and continued by reacting sodium carboxylate with chloride salt of manganese. First reaction and second reaction were conducted at 80-85°C and under perfect agitation. Second reaction took place well in the low concentration of manganese chloride, about 0.25 M or less. Manganese carboxylates (manganese laurate, manganese palmitate, manganese stearate) densities are 0.376, 0.227, and 0.201 g/cm3 respectively. Their onset melting points are 104.95, 111.27, 114.69 °C respectively, obtained by Differential Scanning Calorimeter (DSC) test. Thermogravimetric Analyzer (TGA) test have been done on manganese carboxylates to investigate their thermal stabilities. The results obtained in this study have exposed the capacity of manganese carboxylates stability at processing temperature of polyethylene. It was also found that manganese carboxylates were insoluble in water, ethanol, acetone, n-hexane, cyclohexane, benzene, and toluene.

Keywords: pro-degradant additives, plastics, thermal stability, manganese, carboxylates

Introduction

Live without plastic is rather hard to imagine. In everyday activities we rely on plastic items such as milk jugs, eyeglasses, telephones, nylons, automobiles, and videotapes. The steady growth of plastics sales reflects the ability of plastics products to fulfill an increasing number of consumer demands (Lokensgard, 2004). The world's annual production of polymer resins has experienced a steady growth since the beginning of the century, with growth predicted way into the 21st century close to 1.5 million tons per year in 2000 (Osswald and Menges, 2003). Total resin consumption in Malaysia increased by 8% from 1.6 million MT in 2004 to 1.72 million MT in 2005, of which about 65% were polyolefins (PE & PP). Plastics production systematically increases, thus also plastics waste amount grow (Bajer *et al.*, 2007).

The municipal solid waste stream in the U.S. totals nearly 160 metric tons per year and consists of about 7-11% by weight of post-consumer plastics (Andrady *et al.*, 1993). The increasing utilization of plastics has also caused concern to the role of plastics in environmental pollution. The growing environmental concern has made plastics a target of much criticism due to their lack of degradability (Albertson *et al.*, 1992; Lokensgard, 2004).

Therefore degradable plastics will be important issue to reduce plastics waste amount. Many researches have been done to obtain methods which can improve degradability of plastics.

However, the large amounts of plastics ending up in the waste stream, has resulted in a trend towards manufacture and development of plastics with accelerated degradation. Some methods are used to accelerate the degradation process are the addition of transition metal pro-oxidants or carbon monoxide polymer, both of which are designed to catalyse photo degradation and thermal degradation times (Barr and Kumarakulasinghe, 1994).

Additives and compound are usually tested using TGA and DSC to obtain their thermal stabilities and melting points (Xia *et al.*, 2006; Rimez *et al.*, 2008). Additives must have thermal stability at the processing temperature of resin.

Materials and Methods

Materials

Manganese chloride tetrahydrate (Systerm), sodium hydroxide, lauric acid, palmitic acid, and stearic acid (Merck), ethanol (industrial grade), acetone, n-hexane (R&M Chemicals), cyclohexane, benzene (Merck), and toluene (Systerm) were used without any treatments. Deionized water was used for all processes.

Synthesis of manganese carboxylates

Manganese carboxylates were synthesized in the same manner with synthesis of cobalt (II) linolenat, cobalt (II) oleat. Cobalt (II) linolenat and cobalt (II) oleat could be

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produced by metathesis reaction of cobalt salt solutions and the sodium salt of the organic acid as reported by Grant (1991).

Manganese carboxylates, namely manganese laurate, manganese palmitate, and manganese stearate, were synthesized through two steps of reactions First step, carboxylic acids (lauric acid, palmitic acid, and stearic acid) were reacted with sodium hydroxide to produce sodium carboxylates (sodium laurate, sodium palmitate, and sodium stearate).

These reactions took place in liquid phase at 80-85 °C. Carboxylic acids were melted and added gradually with sodium hydroxide 0.25 M under agitation for one hour. The amount of carboxylic acids and sodium hydroxide were reacted in stoichiometric ratio. Perfect agitation was needed to reach a complete reaction.

The second steps, sodium carboxylates (sodium laurate, sodium palmitate, and sodium stearate) were reacted with manganese chloride to produce manganese carboxylates (manganese laurate, manganese palmitate, and manganese stearate). The synthesis of manganese carboxylates were conducted by adding manganese chloride hexahydrate solution 0.20 M into the product of first step reaction which contains sodium carboxylates. Manganese chloride solution was added gradually. The reaction temperature was maintained at 80-85 °C, with continuous stirring.The solid produced in second step was filtered and washed with hot water to separate sodium chloride. Finally, the solid was dried in the oven at 60 °C for 2 hours

Characterization of manganese carboxylates

The characterization comprises bulk density, solubility, melting point, and degradation temperature. Bulk density test was done using volumetric cylinder. The cylinder was filled with the sample. The excess material on top of the measuring cylinder was scraped off. The sample and the cylinder were then weighed and bulk density was determined by calculating the weight divided by volume. The solubility was tested in various solvents. The solvents used were ethanol, n-hexane, cyclohexane, acetone, benzene, and toluene.

Evaluation of degradation temperatures were done using Thermogravimetric Analyzer (TGA) Q500 from TA Instruments, in N_2 atmosphere, ramp method, heating rate 20 °C/min, and final temperature 1000 °C (Bajer *et al.*, 2007; Gómez *et al.*, 2008). Melting points were investigated using Differential Scanning Calorimeter (DSC) Q1000 from TA Instruments, in N_2 atmosphere, at heating rate 10 °C/min, and temperature range 30-200 °C.

Results and Discussion

Synthesis of manganese carboxylates

Synthesis of manganese carboxylates comprises two steps of reactions. The first step is to produce sodium carboxylates through the reactions which can be stated below.

Lauric acid + sodium hydroxide → sodium laurate + water
Palmitic acid + sodium hydroxide → sodium palmitate + water
Stearic acid + sodium hydroxide → sodium stearate + water

In this reaction, temperature must be controlled at 80-85 °C. The lower temperature would make reaction take place slowly, since the melting point of carboxylic (lauric, palmitic, and stearic) acids are quite high, in the range 44-69 °C. The higher temperature which closes to boiling point of mixture would cause formation of foam. Perfect agitation was needed to ensure mixture in well-mixed condition.

The second reaction could be written as follow:

Sodium laurate + Mn chloride → Mn laurate + sodium chloride
Sodium palmitate + Mn chloride → Mn palmitate + sodium chloride
Sodium stearate + Mn chloride → Mn stearate + sodium chloride

In the second reaction, manganese carboxylates which were produced in solid phase, would form suspension and became hard to be stirred. The low concentration of manganese chloride was favorable since reaction would take place well in low concentration. The low concentration of manganese chloride would make the ratio between solid and liquid low. Thus, mixing process would run well and complete reaction could be reached. Temperature was also kept at 80-85 °C. The higher temperature would initiate flock formation.

Characterization of manganese carboxylates

Bulk Density

Densities of manganese carboxylates are reported in Table 1. All of manganese carboxylates are in the form of powder and have very low density.

Table 1 - Densities of manganese carboxylates

Component	Density, g/cm^3
Manganese laurate	0.376
Manganese palmitate	0.227
Manganese stearate	0.201

Solubility

The solubility of manganese carboxylates in several solvents have been investigated in several types of solvents namely ethanol, n-hexane, cyclohexane, acetone, benzene, and toluene. All manganese carboxylates were insoluble in water and also in all other solvents used. All manganese carboxylates exhibited same property in solubility.

Thermal Stability

Thermal stability of manganese carboxylates were investigated using Thermogravimetric Analyzers (TGA). Degradation temperature could be determined from extreme decrease of weight during heating process. It was shown by steep slope of the curve in TGA test result. The initial and final temperatures of degradation were also obtained from the TGA test result. The results of TGA tests of manganese carboxylates were presented in Figures 1, 2 and 3 respectively. The melting points of manganese carboxylates were depicted in Table 2.

Manganese carboxylates lost more than 80% of their weight during degradation process. The maximum degradation point could also be obtained from Figures 1, 2 and 3. The maximum degradation points were determined from the peaks of curves of relations between derivative weight

change and temperature. TGA test results revealed a single step degradation of all manganese carboxylates.

The degradation temperatures of manganese carboxylates increase with increasing their chains length, from manganese laurate, manganese palmitate, and manganese stearate respectively. The temperatures of maximum degradation also increase in the same manner. The comparisons of degradation temperatures of manganese carboxylates were shown in Figures 4 and 5.

In aging studies for polymeric materials, the decrease in the decomposition and melting temperatures is associated with shorter polymeric chains and a lower thermal stability of the material as reported by Colom *et al.* (2003). It seems similar to phenomenon happened to manganese carboxylates. The shorter chains of manganese carboxylates give the lower thermal stability.

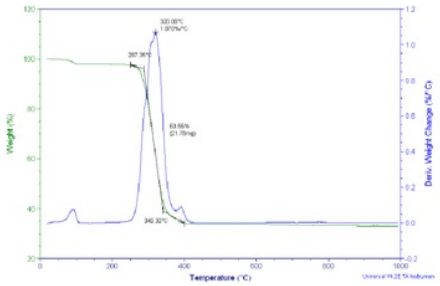

Figure1-TGA and its derivative curve of manganese laurate

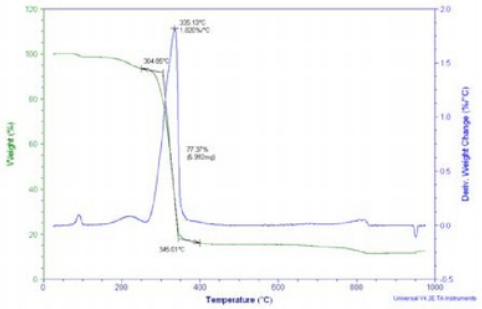

Figure 2 - TGA and its derivative curve of manganese palmitate

Table 2 - Degradation temperatures of manganese carboxylates

Component	Degradation temperature, °C		
	$T_{initial}$	$T_{maximum}$	T_{final}
Manganese laurate	287.35	320.08	340.30
Manganese palmitate	304.85	335.13	345.01
Manganese stearate	312.56	348.68	358.33

Manganese laurate starts to degrade at temperature 287.35 °C. Manganese palmitate and stearate have higher degradation temperatures than manganese laurate. Mixing of additives and polyethylene are usually formed at temperature around 170-190°C (Albertson *et al.*, 1992; Bikiaris *et al.*, 1997; Xia *et al.*, 2006; Bajer *et al.*, 2007). It means that all manganese carboxylates have good thermal stability, especially in application for polyethylene, since the temperature of polyethylene processing is much lower than their degradation temperatures.

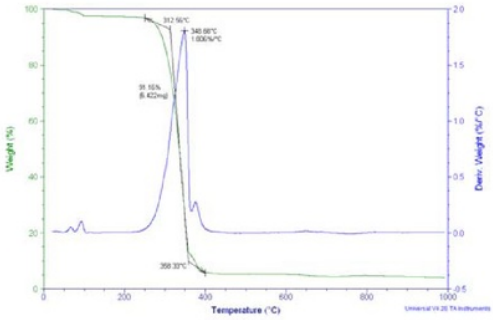

Figure 3 - TGA and its derivative curve of manganese stearate

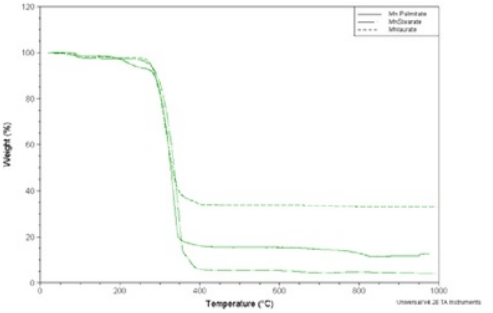

Figure 4 - Comparison of the TGA curves of manganese carboxylates

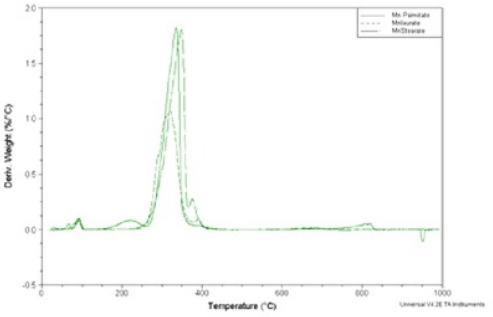

Figure5 - Comparison of the TGA derivative curves of manganese carboxylates

Melting Point

Tests have been done using Differential Scanning Calorimeters (DSC) to determine melting point of

manganese carboxylates. The DSC test results can be seen in Figures 6, 7, and 8.

The melting points of manganese laurate, manganese palmitate, and manganese stearate were determined from the peak of endothermic melting transition. In the calorimetric study performed by DSC, the melting onset temperature (T_o) and the melting peak temperature (T_p) of material could be obtained as reported by Colom *et al* (2003). Melting points of manganese carboxylates were summarized as listed in Table 3 below.

Table 3 - Melting points of manganese carboxylates

Component	Melting Point	
	T_o(°C)	T_p(°C)
Manganese laurate	104.95	108.11
Manganese palmitate	111.27	115.09
Manganese stearate	114.69	117.66

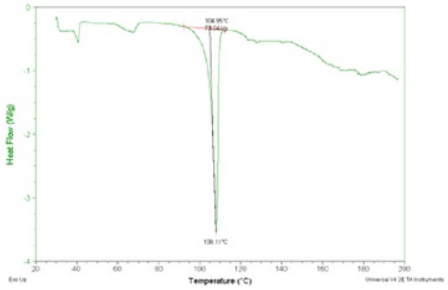

Figure 6 - DSC curve of manganese laurate

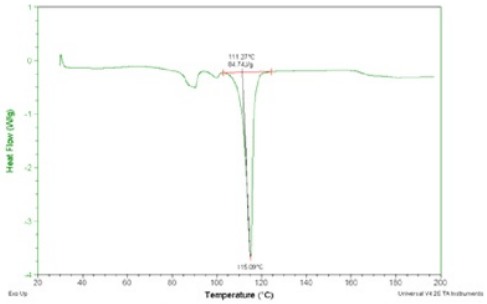

Figure 7 - DSC curve of manganese palmitate

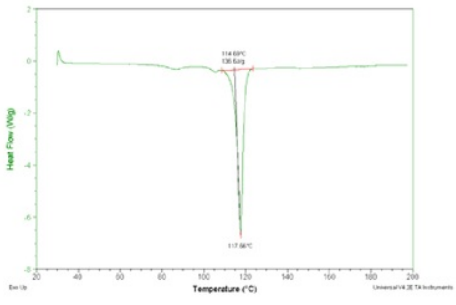

Figure 8 - DSC curve of manganese stearate

Melting points of manganese carboxylates increased with increasing carbon chain length of carboxylates. The increase of melting points is not linear as increasing chain length. As discussed in section of thermal stability, melting points of manganese carboxylates show the similar behavior with polymeric material. The shorter chains of manganese carboxylates give the lower melting point.

Conclusion

Synthesis of manganese carboxylates can be conducted through reaction of sodium carboxylates and cobalt chloride. Thermal stabilities of manganese carboxylates increase with increasing the length of carbon chain, as indicated by temperature of degradation. Manganese carboxylates also have thermal stability at temperature of polyethylene processing. The melting points of manganese carboxylates also increase with increasing the length of carbon chain.

Acknowledgement

Authors would like to thank to Universiti Malaysia Pahang, Ministry of Higher Education for providing financial support through GRS grant.

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